Measurement and simulation of herbicide transport from the corn phase of three cropping systems

F. Ghidey, P.E. Blanchard, R.N. Lerch, N.R. Kitchen, E.E. Alberts, and E.J. Sadler

ABSTRACT: Soils that naturally have a significant runoff component because of low permeability, such as claypans or steep slopes, are especially susceptible to herbicide losses in runoff. For these soils, seasonal losses as impacted by management practices are not well quantified. The objectives of this study were to evaluate the effect of three cropping systems on herbicide loss in surface runoff and develop a model that calculates herbicide concentration. Cropping System 1 (CS1) was a mulch tillage corn-soybean rotation system with herbicides surface applied then incorporated. Cropping System 2 (CS2) was a no-till corn-soybean rotation system with herbicides surface applied and not incorporated. Cropping System 5 (CS5) was a no-till corn-soybean-wheat rotation system with split herbicide application in 1997 and 1999 and no incorporation. The study was conducted on 0.37 ha (0.92 ac) plots equipped with flumes and automated samplers. During each runoff event, runoff volumes were measured, and water samples were collected at equal flow increments and analyzed for atrazine [2-chloro-4-ethylamino-6-isopropylamino-s-triazine] and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethy/acetamide]. Averaged over years, atrazine and metolachlor losses from CS2 were 2.2 and 1.6 times those from CS1, respectively. Atrazine loss to surface runoff from CS1, CS2, and CS5 accounted for 1.6, 2.5, and 5.7% of the total atrazine applied, respectively. Metolachlor loss to surface runoff accounted for 1.8, 2.0, and 2.0% of the total applied for the three cropping systems. Herbicide concentrations were extremely high in the first runoff event measured after application, particularly when it occurred within a few days after application. A generalized model was developed to account for the effects of time after application, runoff volume, and application rate on herbicide concentration in runoff. Overall, the study showed that accounting for incorporation, split application, runoff volume, and timing of runoff events relative to the day of application can increase the confidence in calculations of the amount of herbicide transported to surface runoff.

Keywords: Atrazine, metolachlor, mulch tillage, no-till, water quality

Herbicide use for weed control generally results in increased yield; however, its effect on surface and ground water quality is a major concern. In the Midwest, the loss of herbicides and nutrients to surface water is a more serious problem than transport to ground water (Thurman et al., 1992; Burkhart and Koplin, 1993; Lerch et al., 1998; Blanchard and Donald, 1997). Herbicide transport in surface runoff can be influenced by several factors including tillage type, residue management, incorporation, rate of application, timing of the runoff event relative to herbicide application, and the runoff potential of soils.

Tillage systems such as no-till and chisel tillage methods can substantially reduce soil losses compared to conventional systems (Siemens and Oschwald, 1976; Laflen et al., 1978; Johnson and Moldenhauer, 1979; McGregor and Greer, 1982). However, investigations on the influence of tillage on runoff were not consistent. Most studies have shown that tillage systems that leave residue on the soil surface reduce surface runoff (e.g. Laflen et al., 1978; Larson et al., 1978; Johnson and Moldenhauer, 1979; Langdale et al., 1979; McGregor and Greer, 1982). It could be expected that reduced runoff would have correspondingly reduced herbicide transport. For instance, Baker and Johnson (1979) reported that conservation tillage (no-till and chisel) decreased herbicide losses because of the reduction in runoff and soil losses compared to conventional tillage. In contrast, other studies have indicated that surface residue does not always reduce runoff, particularly in no-till systems (Mannering et al., 1975; Siemen and Oschwald, 1976; Lindstrom et al., 1981; Ghidey and Alberts, 1998). Therefore, in some cases, conservation tillage that leaves residue on the soil surface might increase herbicide loss to surface runoff. Furthermore, residues intercept herbicides applied on the surface, which could easily be washed off and transported in runoff (Martin et al., 1978; Kenimer et al., 1987).

Extraction and transport of chemicals to surface runoff during a rainfall event occur from the upper 2 cm (0.8 in) layer of the soil (Donigan et al., 1977; Frere et al., 1980; Ahuja and Lehman, 1983). Therefore, incorporation below this mixing zone could significantly reduce herbicide loss to surface runoff. Hall et al. (1983) reported that atrazine runoff losses during the growing season under natural rainfall were reduced by 74 percent by incorporation into the surface 5 cm (2 in). In a literature review of pesticide transport in surface runoff, Capel et al. (2001) found that herbicides applied to the soil surface had higher relative losses than soil-incorporated herbicides. They suggested that incorporation of herbicides is the simplest and most effective means of reducing herbicide transport in surface runoff.

Rate of application also affects herbicide loss to runoff. Reducing herbicide application rate reduces herbicide transport to runoff (Hall et al., 1972; Baker and Mickelson, 1994; Hansen et al., 2001). Hall et al. (1972) reported that runoff of atrazine with sediment and water under natural rainfall was nearly directly proportional to the amount applied. To reduce the vulnerability of herbicides to surface runoff after a large application, split

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applications of herbicide have been used.

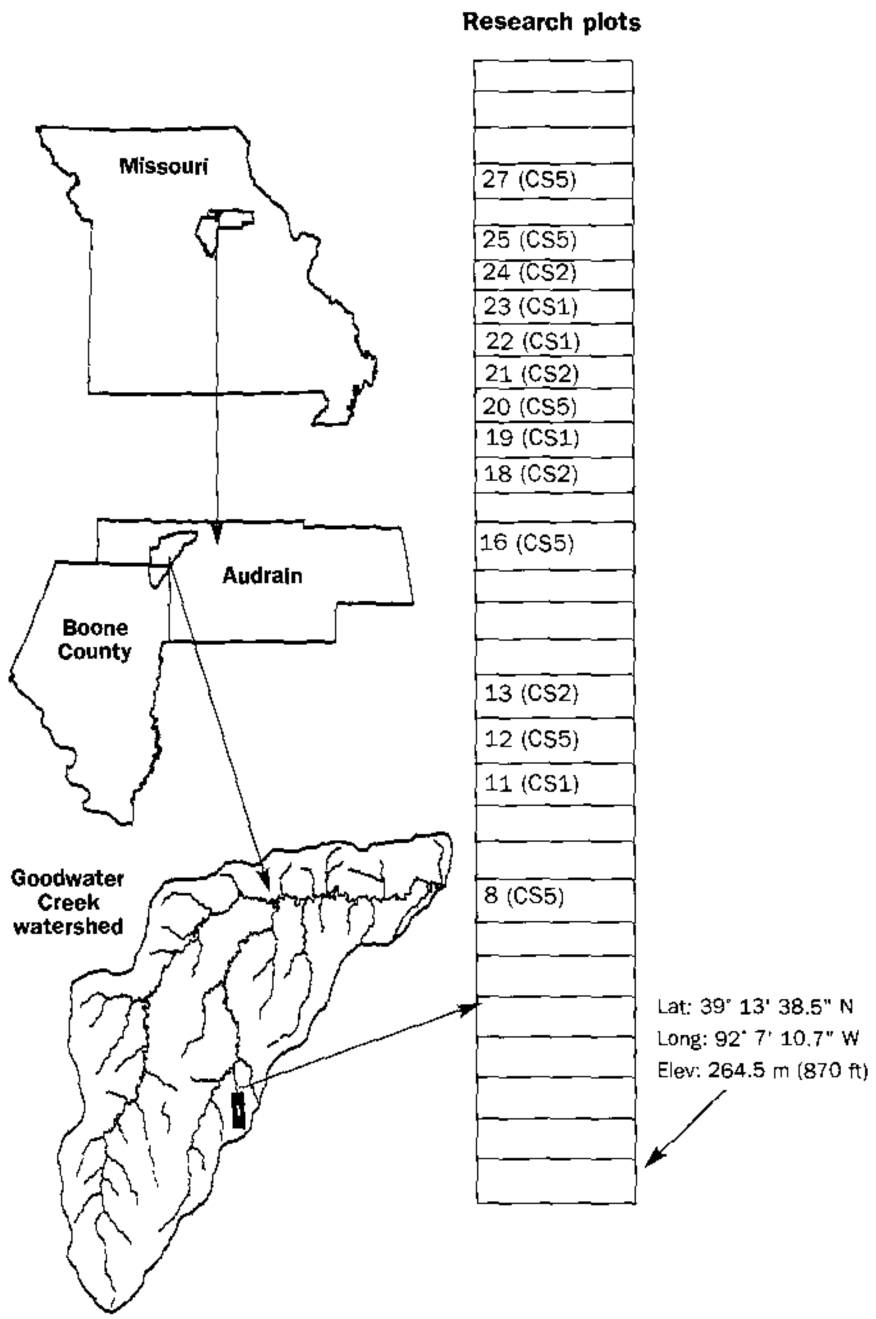
Regardless of herbicide application rate or application method, herbicide concentrations in surface runoff can be very high when runoff events occur shortly after application (Fawcett et al. 1994; Shipitalo et al., 1997; Hansen et al., 2001). Herbicide concentration in the top soil profile from a 35 ha (87 ac) field showed an exponential decay relationship between atrazine concentration and days after application (Ghidey et. al. 1997); however, the relationship was not reported in the paper. An exponential decline in soil concentration suggests that the amount of atrazine available for transport in runoff likely declines at a similar rate. Most previous studies relate herbicide concentration in surface runoff to time elapsed after application (Triplett et al., 1978; Gaynor et al., 1995; Shipitalo et al., 1997).

Soils that naturally have a significant runoff component because of low permeability and/or steep slope are especially susceptible to soil and herbicide losses with runoff, such as the claypan soils of the U.S. Midwest (MLRA 113) (USDA Soil Survey, 1992). Within this region, Ghidey and Alberts (1998) reported long-term effects of cropping systems on surface runoff and soil loss. No-till significantly increased surface runoff and substantially reduced soil loss when compared to conventional and chisel tillage systems. Lerch and Blanchard (2003) reported that runoff potential of soils was a critical factor in determining watershed vulnerability to herbicide transport. However, little documentation is available on the impact of cropping and management on herbicide transport from these soils.

The Missouri Management Systems Evaluation Areas project was initiated in 1991 to develop environmentally sound, economically profitable, and socially acceptable cropping systems and technologies for claypan and claypan-like soils (Ward et al., 1994). This project evolved into the Agricultural Systems for Environmental Quality project in 1996. As part of Missouri's Management Systems Evaluation Areas and Agricultural Systems for Environmental Quality projects, plot-scale studies were used to evaluate the effects of cropping systems on yield, crop N uptake, and transport of agrichemicals to surface water.

The objectives of the investigation reported here were: 1) to evaluate the effects of corn herbicide application methods and rates and application timing on surface water quality, and 2) to develop equations to calculate herbicide concentrations in surface runoff as a function of application rate, runoff volume, days after application, and herbicide placement.

Figure 1
Location of the research plots. The correspondence of plots and years during which samples were collected are presented in Table 1.



Methods and Materials

Study area. The study was located in the Goodwater Creek watershed, a 7250 ha (17908 ac) agricultural area in the claypan soil region of north-central Missouri (Figure 1). Predominant soils are Vertic Epiaqualfs, Vertic Albaqualfs, and Vertic Epiaqualfs of the Mexico, Adco, and Leonard series, respectively (http://soils.usda.gov/technical/classification/). The mapping units in this specific study belong to the Mexico claypan soils, which are considered poorly drained because of a naturally occurring argillic claypan hori-

Table 1. Tillage and herbicide management plots planted to corn.

Year	Cropping system	Planting date	Herbicide†	Rate kg ha^{-1}	Method of application	Date of application
1997	CS1	05-13	Atrazine	2.24	Broadcast, incorporated	05-13
	(19,22)‡		Metolachlor	1.12	Broadcast, incorporated	05-13
	CS2	05-12	Atrazine	2.24	Broadcast, not incorporated	05-12
	(13,24)		Metolachlor	1.12	Broadcast, not incorporated	05-12
	CS5	05-16	Atrazine	1.12	Broadcast, not incorporated	05-01
	(8,16)		Atrazine	0.56	Broadcast, not incorporated	06-13
1998	CS1	05-21	Atrazine	2.24	Broadcast, incorporated	05-21
	(11,23)		Metolachlor	1.42	Broadcast, incorporated	05-21
	CS2	05-21	Atrazine	2.24	Broadcast, not incorporated	05-21
	(18,21)		Metolachlor	1.42	Broadcast, not incorporated	05-21
	CS5	05-21	Atrazine	0.85	Broadcast, not incorporated	06-25
	(20,25)					
1999	CS1	06-03	Atrazine	2.24	Broadcast, incorporated	06-03
	(19,22)		Metolachlor	1.42	Broadcast, incorporated	06-03
	CS2	06-03	Atrazine	2.24	Broadcast, not incorporated	06-03
	(13,24)		Metolachlor	1.42	Broadcast, not incorporated	06-03
	CS5	06-03	Atrazine	2.24	Broadcast, not incorporated	06-03
	(12,27)		Metolachlor	1.17	Broadcast, not incorporated	06-03
			Atrazine	0.85	Broadcast, not incorporated	06-25
2000	CS1	05-16	Atrazine	2.24	Broadcast, incorporated	05-16
	(11,23)		Metolachlor	1.42	Broadcast, incorporated	05-16
	CS2	05-16	Atrazine	2.24	Broadcast, not incorporated	05-16
	(18,21)		Metolachlor	1.42	Broadcast, not incorporated	05-16
	CS5	05-15	Atrazine	1.12	Broadcast, not incorporated	06-08
	(8,16)		Metolachlor	0.71	Broadcast, not incorporated	06-08
2001	CS1	05-16	Atrazine	2.24	Broadcast, incorporated	05-16
	(19,22)		Metolachlor	1.87	Broadcast, incorporated	05-16
	CS2	05-16	Atrazine	2.24	Broadcast, not incorporated	05-16
	(13,24)		Metolachlor	1.87	Broadcast, not incorporated	05-16
	CS5	05-17	Atrazine	0.56	Broadcast, not incorporated	06-13
	(20,25)		Metolachlor	0.85	Broadcast, not incorporated	06-13
2002	CS1	05-31	Atrazine	2.24	Broadcast, incorporated	05-31
	(11,23)		Metolachlor	1.87	Broadcast, incorporated	05-31
	CS2	05-31	Atrazine	2.24	Broadcast, not incorporated	05-31
	(18,21)		Metolachlor	1.87	Broadcast, not incorporated	05-31
	CS5	05-31	Atrazine	0.85	Broadcast, not incorporated	06-17
	(12,27)		Metolachlor	0.85	Broadcast, not incorporated	05-31

† Other herbicides (pre-plant, at planting, or post plant) may have also been used to control weeds, but are not reported here because they were not part of the water quality monitoring.

‡ Numbers in parenthesis are plot numbers.

zon located 15 to 45 cm (6 to 18 in) below the surface. The clay content of the argillic horizon is generally greater than 50 percent and the clays are primarily smectites.

Cropping and management systems. In on-going long-term research (1991 to present), six cropping systems have been evaluated on thirty 0.374 ha (0.92 ac) plots [18 m (65 ft) wide by 189 m (620 ft) long], in a randomized complete block design with three replications. Plot slopes range from 0 to 2 percent. In spring 1991 when plots were laid out, berms [1 ft (0.3 m) high x 5 ft (1.5 m) wide] running down slope were created along the plot length to ensure no cross-plot contamination of surface runoff. In fall 1991, trenches were dug along the top of these berms and were lined with plastic to prevent subsurface flow between plots.

Due to limitations related to topography of the experimental area, only two replications of these cropping systems could be instrumented to measure the quantity and quality of surface runoff. Cropping System 1 (CS1) was a mulch tillage corn-soybean rotation system. Mulch tillage consisted of fall chisel plowing and field cultivation both before and after herbicide application for seedbed preparation and herbicide incorporation. Cropping System 2 (CS2) was a no-till corn-soybean rotation system. Cropping System 5 (CS5) was a no-till corn-soybean-wheat rotation system. The weed management system for the CS5 system was adaptive, meaning scouting of weed species and intensity dictated herbicide type, rate, and timing. The result of this was a varied herbicide application from year to year. In 1997 and 1999, this adaptive system resulted in split herbicide applications. In the long-term experiment, each cropping phase of a cropping system was represented within each block. However, for this study, surface runoff was measured and runoff samples were collected only from plots that were planted to corn. Tillage and herbicide management for CS1, CS2, and CS5 when planted to corn are presented in Table 1. Crop rotation prevented samples being collected from the same plots every year (see Table 1 for plot numbers by year and cropping system).

Instrumentation. In 1996, the outlets of the plots were instrumented with Parshall flumes and automatic samplers to measure runoff volume and collect runoff samples for chemical analysis. The flumes were ASTM-standard Parshall flumes (Culverts & Industrial Supply Co., Mills, Wyoming[1]), with nominal 0.1524 m (6 in) throats, and were installed according to manufacturer's specifications. These were left in place for the six-year duration of the experiment, requiring a total of 14 flumes for the three cropping systems. The lower end of the plots required a collector wall or wing wall to route runoff through the flume. These wing walls were installed after planting each year. In 1997, this wall was constructed of removable interlocking concrete sections with a 0.15 m (5.9 in) blade extending into the soil beneath them (four plots), and straw bales anchored with metal rods into the soil (two plots). Plastic sheeting lined the upper face of both wing wall types. During the years 1998–2002, this wall was comprised of sheet metal sections [1.5 ft high x 29 ft wide [(0.46 m high x 8.8 m wide], 2 per side] screwed to a board bolted to the top of a 0.9 m (36 in) concrete wall installed below grade, with all seams caulked.

A stilling well was installed external to the flume on the side wall, with ports penetrating the flume wall and the wall of the stilling well. The well extended 6.7 cm (2.63 in) below the floor of the flume, to keep the pressure sensor (Hach Company, Loveland, Colorado) submerged. The full-scale range of the sensor was 1.8 m (6 ft), with stated accuracy of 0.2 percent. Because the sensor was being applied at the extreme low end of the range during low-flow events, thermal errors and sensor drift were not negligible. Sensor drift was corrected by extending the baseline of the head measurement at the end of the event back to the beginning of the event to obtain a corrected head, which was then used to compute flow.

The manufacturer provided the standard calibration equation for the nominal flume size. However, the width of the flumes was determined to be 6 mm (0.236 in) larger than the manufacturers stated width; thus, the equation used to compute flow was adjusted accordingly (Allen Hjelmfelt personal communication, 1996) to give the following equation.

$$Q = 0.3936 \times H^{1.56} \qquad (1)$$

where,

Q = discharge in $m^3 s^{-1}$

H = head above the crest of the flume in meters

Automated samplers (Sigma 900MAX, Hach Company, Loveland, Colorado) with the pressure transducer mentioned above were installed annually right after planting. The study was designed to be able to sample up to a 5.08 cm (2 in) runoff event. Each sampler had eight bottles, and each bottle collected up to 6.35 mm (0.25 in) of runoff. To capture small events, up to nine subsamples were collected into each bottle, each representing 0.0706 mm (0.0278 in) of runoff. The samples were transported under refrigeration back to the laboratory. As previously indicated, only runoff events that occurred from the date of herbicide application to grain harvest were collected for this study.

To measure climatic variables, a weather station was located adjacent to the plot, including rainfall in a gauge (Belfort Instrument Company, Baltimore, Maryland) modified with a load cell and data logger. Rainfall was directed through a 20 cm (7.9 in) diameter collecting ring and funnel to a bucket resting on the surface of the load cell that was connected to the data logger for recording rainfall volumes every two minutes.

Herbicide has been known to be deposited with rainfall (Hatfield et al., 1996). To measure herbicide concentrations, rainfall was sampled with a wet/dry precipitation sampler (Model 301, Aerochem Metrics, Inc. Bushnell, Florida). This sampler has a sensor pad that opened the cover to expose the collection container. The sensor pad was also heated to dry the sensor quickly after a rainfall event to close the cover. Precipitation samples were usually collected and transported under refrigeration to the laboratory within 24 hour of an event. Dry deposition was not analyzed for herbicides.

Runoff and herbicide data are reported in this paper on an event basis. There were instances where rainfall events separated by a non rainfall period of a few hours that produced hydrographs with multiple peaks. If the hydrograph from the first event fell off or recessed to zero, then multiple runoff events were considered to occur. Runoff from multiple events was combined if one of the events had an insufficient discharge rate to activate the pumping sampler, if only one herbicide concentration data was measured for both events, or if only one of three cropping systems had multiple events.

Herbicide analysis and load computation. As described previously, cropped area of the plots were separated by non-cropped 1.52-m (5-ft) wide berms. The drainage area of each plot, including the cropped and non cropped area, was 0.3744 ha (0.925 ac). Herbicides were not applied to the berms, thus the treated area of each plot was 0.3456 ha (0.854 ac). As runoff occurred, herbicides were transported from the treated area and diluted by runoff from the berm area. Concentrations reported in this manuscript were those measured in the laboratory, and are 8.3 percent lower than those expected if the drainage and treated areas were the same.

Samples were refrigerated until processing. All samples were filtered through 0.45 μm nylon filters and analyzed for atrazine and metolachlor using enzyme-linked immuno sorbent assay (ELISA) (Strategic Diagnostics Inc. (SDI), Warminster, Pennsylvania). Limits of detection were 0.05 $\mu g\ L^{-1}$ for both herbicides. Runoff samples from the first two events were diluted as needed to insure that concentrations fell within the linear range (0.05 - 5 $\mu g\ L^{-1}$) of the ELISA kits.

For each event, individual sample concentrations were multiplied by corresponding runoff volumes to calculate herbicide load:

$$L_t = C_t \times Q_t \qquad (2)$$

where,

L_t = herbicide load for the sampling period t (µg)

C_t = herbicide concentration in the runoff for sampling period t ($\mu g\ L^{-1}$)

Q_t = the volume of runoff measured during the sampling period t (L).

Q_t and L_t were then integrated to calculate event total runoff and herbicide load. Runoff depths for each event were calculated by dividing the runoff volume by the drainage area (0.3744 ha), while herbicide losses ($g\ ha^{-1}$) were calculated by dividing the computed load by the treated area (0.3456 ha). Event based herbicide concentrations representative of the treated area could have been computed using runoff and herbicide losses assuming that runoff from the treated and drainage areas were the same. However, this approach was not chosen because we wanted to use measured data in preparing tables and figures, recognizing that herbicide concentrations were conservative.

Event-based statistical analysis. As previously mentioned, CS1 was in a mulch tillage system where herbicides were surface applied and incorporated, and CS2 was in a no-till system where herbicides were surface applied and not incorporated. Dates and rates of application for both CS1 and CS2 were the same, thus individual events could be compared. Data measured from CS5 was not included in this analysis because CS5 had different herbicide application rates and dates than did CS1 and CS2. For individual events, runoff and concentration data measured from CS1 and CS2 during 1997 to 2002 (excluding 2001) were used to evaluate the effect of tillage and incorporation on herbicide loss to surface runoff. Statistical analysis (GLM) with a complete randomized block design was used in this analysis (SAS, 2001). The block by cropping system interaction was used as the error term, with one degree of freedom. As mentioned before, the study had only two replications. Limitations inherent to the experimental design (including the size and physical layout of plots) resulted in a high degree of variability, especially associated with measurement of runoff volume. These limitations also resulted in high critical values of t. Therefore, results for runoff, concentration, and loss are reported accompanied by p values. This allows the reader to judge the significance of the results.

Seasonal statistical analysis. Throughout the study period, about 10 percent of the runoff events could not be measured for several reasons, including scouring under the flume causing bypass flow, crop residue clogging the flume, and occasional sampler malfunction. However, to compute seasonal differences in measured runoff and herbicide loss, these missing values must be estimated. Linear regression relationships for runoff values and atrazine and metolachlor concentrations were developed between blocks. As previously mentioned, due to crop rotation, samples were not taken from the same plots every year. For instance, CS1 samples were collected from plots 19 and 22 in 1997, 1999, and 2001; and from plots 11 and 23 in the other years. Thus, missing values for plot 22 were estimated from measured values from plot 19, and vice versa. For each of the three cropping systems, the correlation of runoff between the blocks was quite high, with r^2 values greater than 0.90. Correlation of herbicide concentrations was also high, with r^2 values greater than 0.85.

Statistical analysis (GLM) was also used to evaluate the effects of the three cropping systems (CS1, CS2, and CS5) on seasonal runoff and herbicide losses. Although CS2 and CS5 were both in a no-till tillage system where herbicides were surface applied and not incorporated, CS5 had split herbicide application in 1997 and 1999. Also, throughout the study period, herbicide amount applied to CS5 was often different than that applied to CS2. Seasonal herbicide losses from CS2 and CS5 were statistically analyzed to evaluate the effects of split herbicide application and rate of application on herbicide losses to surface runoff. This analysis, being a three-way comparison, was done using an F-protected LSD mean comparison at $\alpha = 0.10$. Individual two-way comparisons are reported in the text along with their p-values.

Modeling herbicide concentration. Most of the studies related to herbicide transport in surface runoff are conducted at a plot or field scale. Conducting experiments at a watershed scale to evaluate the effects of all the aforementioned factors on herbicide transport would be difficult, expensive, and time-consuming. A model that accounts for these factors would be more likely to be transferable to other settings, management practices, and weather patterns.

Herbicide concentration in surface runoff has been expressed by an exponential equation as follows:

$$[C] = [C_o] \times e^{-(k \times t)} \qquad (3)$$

where,

[C] = computed herbicide concentration

$[C_0]$ = the initial concentration, and t is days after herbicide application.

However, as discussed previously, rate of application and runoff volume are both important factors that influence herbicide concentration and loss in surface runoff. Therefore, the exponential model was modified to account for these parameters as follows:

$$[C] = a \times \left(\frac{R}{Q}\right) \times e^{-(k \times t)} \qquad (4)$$

where,

[C] = Computed atrazine or metolachlor concentration ($\mu g\ L^{-1}$)

R = Herbicide application rates ($\mu g\ ha^{-1}$)

Q = Runoff measured for the events ($L\ ha^{-1}$)

t = Time after herbicide application, days

a, k = Coefficients

This equation has several advantages. For instance, it can be rearranged to compute herbicide loss in $\mu g\ ha^{-1}$:

$$Loss = [C]Q = a\,R\,e^{-(k \times t)} \qquad (5)$$

Further, it can also be rearranged to compute percent of herbicide applied transported in surface runoff:

$$\%\ applied = 100 \times \frac{[C]\,Q}{R} = 100 \times a\,e^{-(k \times t)} \qquad (6)$$

The Non-Linear procedure of SAS (Proc NLIN) was used to estimate the coefficients a and k for CS1 and CS2.

Potential errors in primary measurements. Potential errors are unavoidable with field studies of this type. The intent of this section is to discuss these potential errors and analyze how they propagate through the calculation of runoff volume and herbicide load (Equations 1 and 2). Furthermore, because our experimental design was limited to two replications, additional information regarding the confidence and accuracy of our primary measurements was warranted.

For this study, most of the errors due to physical design, including leaks in the wing walls, flume clogging by crop residue, and run-on to the plots, were either detectable, in which case the data were removed, or considered negligible. Therefore, this section focuses on the two potential sources of measurement error: runoff volume and herbicide concentration analysis. Uncertainty analysis (Holman, 1978) was performed to evaluate these errors.

Runoff measurements and calculations were subject to instrumental errors including head measurement by the pressure transducer and inaccuracy of the Parshall flume head-flow rate relationship (Equation 1). Based on the manufacturer's specifications, the estimated maximum error associated with the head measurement was ± 2.0 mm (0.08 in). The manufacturer's specification for Parshall flumes indicated that the flumes were accurate to within ± 3.0 mm (0.12 in). Using these errors for the head measurements over the range of 37 to 366 mm (0.12 to 1.2 ft), uncertainty analysis of Equation (1) yielded relative errors in the range of 3.3 to 8.3 percent for the computed runoff volume. Since high volume runoff events also correspond to high head measurements, the error associated with the majority of the seasonal runoff would be at the low end of this range.

Herbicide analyses in the laboratory were accurate to within ± 0.05 and ± 0.5 μg L^{-1} for undiluted and diluted concentrations, respectively, for both atrazine and metolachlor, as determined by repeated measurements of analyte standards (Strategic Diagnostics Inc., Warminster, Pennsylvania). Errors associated with sample dilution were no greater than ± 0.01 mL. For the metolachlor kit, there were no cross-reacting compounds present in the runoff water. However, the atrazine kits did have significant cross-reactivity with the atrazine metabolite, deethylatrazine (DEA) [2-chloro-4-amino-6-isopropylamino-s-triazine], the major atrazine metabolite in surface runoff (Thurman et al., 1994). Cross-reactivity errors for atrazine ranged from ±0.56 μg L^{-1}at about 40 days after application to ±2.75 μg L^{-1}at application. Uncertainty analysis of the atrazine measurements for 40 days after application, when relative cross-reactivity would be significant, showed that the relative measurement errors at this point in the growing season were slightly lower than for events within seven days after application. Using the above stated errors for runoff volume and herbicide concentrations, the uncertainty analysis of Equation (2) can be performed. For example, using a 12.3-mm (0.48-in) runoff event fourteen days after application for which the reported atrazine concentration was 224 μg L^{-1} and the reported metolachlor concentration was 254 μg L^{-1}, the estimated error in the load for both herbicides was 10.7 percent (± 1.1 g for atrazine and ± 1.2 g for metolachlor).

Table 2. Annual and seasonal precipitation measured from 1997 to 2002.

Year	Annual precipitation (mm)	Seasonal (May-Sept) precipitation (mm)
1997	941	414
1998	1158	625
1999	824	288
2000	926	602
2001	1029	504
2002	860	440
Mean	956	479
Long-term mean (1970 to 2003)	944	500

Results and Discussion

Precipitation. Annual and seasonal precipitation from the study area is given in Table 2. During the six seasons, from 36 to 65 percent of the annual rainfall occurred during the growing season compared to the long term (34 year) average of 53 percent. Seasonal precipitation was above the long-term average in 1998 and 2000 and below the long term average in 1997, 1999, and 2002. Rainfall that occurred during the 1997, 1999, and 2002 growing seasons resulted in very few runoff events.

Rainfall samples were collected from 1997 to 2002 to measure herbicide concentrations in precipitation. Atrazine and metolachlor concentrations in precipitation were extremely low (< 0.1 μg L^{-1}) and represented only 0.22 percent of atrazine and 0.77 percent of metolachlor measured in surface runoff in this study. Therefore, herbicide contribution for rainfall was considered negligible.

Event-based runoff. Surface runoff measured for the events that occurred from 1997-2002 are shown in Table 3 and 4. The 2001 data was not included because, due to corn stand failure and replanting, runoff was not measured from the plots under CS2 until 36 days after the chemical application date. In 1997, four small runoff events were measured, and for each of the events runoff from CS2 was more than three times that from CS1. For events measured in 1998 to 2002 there was little difference in surface runoff between CS1 and CS2.

Seasonal runoff. Seasonal runoff measured from CS1, CS2, and CS5 is given in Table 3. In 1997, total runoff measured from CS2 and CS5 was 3.7 times ($p = 0.05$) and 2.2 times ($p = 0.16$), respectively, greater than that from CS1. In 1998, runoff from CS5 was 76 percent ($p = 0.02$) and 33 percent ($p = 0.02$) higher than CS1 and CS2, respectively. In 2002, runoff from CS1 was 74 percent ($p = 0.06$) and 107 percent ($p = 0.04$) higher than CS2 and CS5, respectively. In 1999 and 2000, runoff values from CS1, CS2, and CS5 were not different ($p<0.10$), and because of replanting of CS2 in 2001, these differences could not be compared. Averaged over the years (excluding 2001), CS2 and CS5 had 13 percent ($p = 0.20$) and 19 percent ($p = 0.11$), respectively, greater runoff than CS1.

In a no-till system, residues are expected to both increase infiltration and prevent the development of surface crusting, which consequently should decrease runoff. However, previous long-term studies had shown that in a claypan soil, no-till increased mean annual runoff by 14 percent compared to conventional tillage systems (Ghidey and Alberts, 1998). This difference was attributed to mulch tillage breaking a sealed soil surface, increasing micro-relief, and drying the soil more quickly, all of which result in increased infiltration and reduced surface runoff. The values in the present study are comparable to the earlier study, which had more years and was significant at $\alpha = 0.05$. In this study, runoff from the two no-till systems was either higher or not different than runoff from the

Table 3. Runoff, atrazine, and metolachlor measured from CS1 and CS2 for the events that occurred in 1997 to 2002.

					Atrazine				Metolachlor			
			Runoff, mm		µg L⁻¹		g ha⁻¹		µg L⁻¹		g ha⁻¹	
Date	DAA	Rainfall (mm)	CS1	CS2	CS1	CS2	CS1	CS2	CS1	CS2	CS1	CS2
05-27-1997	14*	13.5	3.2†	12.3	407.8‡	224.1 (0.19)	13.8	29.8	349.5	253.8 (0.21)	11.8	34.1
05-30-1997	17	11.4	2.3	7.4	351.9	231.2 (0.22)	8.7	17.3	335.2	289.9 (0.27)	8.3	22.5
06-22-1997	40	39.4	5.1	16.6 (0.09)†	28.0	26.4	1.5	4.7	34.9	17.5	1.9	3.1
06-22-1997	40	7.9	1.3	7.6 (0.09)	28.1	41.5	0.4	3.3	35.2	27.1	0.5	2.2
06-08-1998	18	40.6	4.6	9.3 (0.20)	67.5	286.0 (0.20)	3.2	29.8 (0.28)	62.8	109.0 (0.32)	3.1	11.2 (0.33)
06-14-1998	23	34.3	7.2	10.9 (0.16)	18.0	70.6 (0.03)	1.4	8.5 (0.14)	15.2	.	1.2	—
06-22-1998	32	27.1	8.6	9.8 (0.37)	3.8	23.0 (0.17)	0.4	2.5 (0.26)	7.1	15.5 (0.12)	0.7	1.4 (0.23)
06-29-1998	39	80.8	9.0	12.4 (0.42)	2.2	4.1	0.2	0.6	2.6	4.2	0.2	0.5
07-04-1998	44	49.8	16.4	19.9	1.9	5.6 (0.12)	0.3	1.2	3.2	3.7 (0.70)	0.6	0.8
07-07-1998	47	11.7	0.8	0.8 (0.89)	2.0	4.0 (0.33)	0.0	0.0	2.9	2.7 (0.93)	0.0	0.0 (0.87)
07-30-1998	70	44.7	3.0	2.7 (0.55)	0.5	1.1 (0.03)	0.0	0.0 (0.33)	1.7	1.5 (0.80)	0.1	0.0 (0.93)
06-23-1999	20	50.8	16.0	15.2 (0.59)	35.3	48.1 (0.34)	6.1	8.0 (0.50)	33.4	32.7 (0.96)	5.8	5.5 (0.92)
06-30-1999	27	58.7	42.5	42.5	15.1	26.4	7.0	12.0	23.0	15.3	10.6	7.0
05-26-2000	10	41.9	10.1	8.3 (0.11)	180.0	855.8 (0.06)	21.0	80.5 (0.28)	103.1	181.0 (0.37)	12.9	16.3 (0.41)
06-11-2000	26	35.3	11.7	8.0	22.0	155.2	2.7	13.4	14.0	52.4	1.7	4.5
06-14-2000	29	13.7	6.2	3.6 (0.27)	24.4	101.6 (0.05)	1.6	4.0 (0.38)	23.0	29.1 (0.20)	1.5	1.2 (0.59)
06-14-2000	29	7.9	3.9	4.2 (0.84)	28.9	99.0 (0.03)	1.2	4.6 (0.30)	36.4	34.5 (0.93)	1.5	1.7 (0.91)
06-20-2000	35	21.1	7.7	6.7 (0.56)	13.5	35.3 (0.02)	1.1	2.6 (0.21)	9.5	18.3 (0.09)	0.8	1.4 (0.36)
06-20-2000	35	18.3	12.6	14.1 (0.55)	12.1	35.4 (0.05)	1.6	5.4 (0.17)	12.6	19.8 (0.05)	1.7	3.0 (0.16)
06-25-2000	40	21.3	9.0	9.4 (0.94)	4.2	10.0 (0.15)	0.4	1.0 (0.39)	5.9	6.3 (0.88)	0.6	0.7 (0.82)
07-02-2000	47	18.1	2.4	1.2 (0.33)	4.1	11.5 (0.11)	0.1	0.1 (0.77)	7.2	5.7 (0.38)	0.2	0.1 (0.30)
08-07-2000	83	54.4	5.6	6.1 (0.77)	37.5	5.6 (0.07)	2.3	0.4 (0.10)	0.9	1.8 (0.37)	0.1	0.1 (0.34)
08-23-2000	99	53.3	29.0	33.5 (0.67)	0.6	1.0 (0.32)	0.2	0.4 (0.05)	0.5	0.5 (0.63)	0.2	0.2
08-24-2000	100	81.3	68.9	69.1 (0.99)	0.8	1.0 (0.77)	0.6	0.7 (0.63)	0.6	0.6 (0.93)	0.4	0.5 (0.30)
05-17-2001	2	29.7	5.6	—	120.7	—	7.4	—	106.7	—	6.6	—
05-20-2001	5	13.5	6.3	—	358.0	—	24.4	—	360.3	—	24.4	—
05-30-2001	14	46.2	26.3	—	118.7	—	33.7	—	119.1	—	33.3	—
06-01-2001	16	6.9	2.6	—	58.2	—	1.6	—	51.2	—	1.4	—
06-03-2001	18	9.9	2.6	—	43.0	—	1.2	—	34.3	—	1.0	—
06-04-2001	19	37.1	36.6	—	28.4	—	12.4	—	39.7	—	15.9	—
06-06-2001	21	46.0	41.4	—	14.4	—	6.5	—	20.7	—	9.3	—
06-14-2001	29	27.9	8.8	—	5.2	—	0.5	—	28.2	—	2.7	—
06-14-2001	29	5.9	0.7	—	10.6	—	0.1	—	38.8	—	0.3	—
06-21-2001	36	18.0	8.3	9.0	2.0	3.4	0.2	0.4	22.8	1.6	2.0	0.1
07-032001	49	40.6	15.2	8.9	8.0	12.2	1.4	1.2	16.9	0.0	2.8	0.0
08-23-2001	100	32.3	7.9	2.8	0.2	0.1	0.0	0.0	0.7	0.0	0.1	0.0
06-12-2002	12	41.9	8.7	5.0	510.0	801.4 (0.15)	47.7	43.6	85.4	92.2 (0.61)	8.0	4.8

*** In 1997, herbicides were applied to CS2 one day earlier than to CS1, thus DAA for CS2 are 1 day more than those given in the table.**

† Statistical analysis was not performed for the events when regression equations were used to estimate missing data.

‡ Numbers in parenthesis are P-values.

. Data could not be estimated because neither block was sampled

mulch tillage system. Apparently, in these soils, significant development of preferential flow paths does not occur under no-till. Despite expected reductions in soil loss, these no-till systems did not reduce runoff volume from claypan soils.

Event-based herbicide concentrations. Flow-weighted herbicide concentrations for the events that occurred during the study period (1997 to 2002) are shown in Tables 3 and 4 and Figure 2. Measured atrazine and metolachlor concentrations in runoff were extremely high (up to 855 µg L⁻¹ for atrazine and 349 µg L⁻¹ for metolachlor) in the first runoff events after application, particularly when runoff occurred within three weeks after application. Concentrations declined rapidly over the first 30 days following application and were near zero by 60 to 70 days after application. The only exceptions were the atrazine concentration from both samples measured from CS1 for the event that occurred 83 days after application in 2000. Atrazine concentration for this event was 37.5 µg L⁻¹, which was almost nine times higher than the concentrations measured 40 days earlier. We have no explanation for this anomalous concentration. Except for this event, atrazine concentrations in runoff were below the current maximum contaminant level (MCL) for drinking water (3 µg L⁻¹ for atrazine) in the samples collected eight weeks or more after application.

Table 4. Atrazine and metolachlor concentrations and loads measured in runoff from CS5.

Date	DAA	Runoff, mm	Atrazine		Metolachlor	
			µg L-1	g ha-1	µg L-1	g ha-1
05-27-1997	26	5.7	123.9	7.8	——†	——
05-30-1997	29	5.0	123.2	6.7	——	——
06-22-1997	10*	11.9	396.3	51.5	——	——
06-22-1997	10	5.0	361.0	19.5	——	——
06-29-1998	4	23.6	120.9	30.3	——	——
07-04-1998	9	24.0	140.9	36.4	——	——
07-07-1998	12	0.4	113.7	0.5	——	——
07-30-1998	35	6.7	12.8	1.0	——	——
06-23-1999	20	18.4	46.2	9.3	15.9	3.2
06-30-1999	5†	43.1	43.4	20.2	12.8	5.9
06-11-2000	3	3.5	375.0	14.4	95.7	3.8
06-14-2000	6	10.2	281.2	31.4	50.5	5.4
06-16-2000	8	2.1	257.8	5.7	41.0	0.9
06-20-2000	12	8.4	129.3	11.9	16.0	1.4
06-20-2000	12	15.6	108.1	18.7	11.2	2.0
06-25-2000	17	11.7	56.0	7.1	5.0	0.6
07-02-2000	24	1.7	30.7	0.6	5.2	0.1
07-30-2000	52	0.1	68.2	0.1	16.2	0.0
08-07-2000	61	3.6	14.7	0.7	3.0	0.1
08-23-2000	76	30.9	2.9	1.0	0.5	0.2
08-24-2000	77	82.0	1.8	1.5	0.4	0.3
06-14-2001	1	4.2	546.2	24.4	498.1	20.2
06-14-2001	1	2.8	446.1	13.6	331.0	10.1
06-21-2001	8	11.8	113.8	14.8	33.5	4.4
07-03-2001	20	12.0	75.0	10.0	30.0	4.1
07-23-2001	91	2.2	1.3	0.0	0.8	0.0
10-05-2001	114	37.6	1.0	0.4	1.3	0.5
6-12-2002	12***	4.2	——**	——.	24.3	1.1

* Days after second herbicide application.

† Metolachlor was not applied to CS5 in 1997 and 1998.

** No runoff event occurred after atrazine was applied to CS5.

*** This is days after application for metolachlor only.

Atrazine and metolachlor concentrations in runoff from CS2 were higher than from CS1, except for the 1997 events. For the first event in 1997, atrazine and metolachlor concentrations from CS1 were 82 percent ($p = 0.19$) and 52 percent ($p = 0.21$) higher than from CS2. For the second event, atrazine and metolachlor concentrations from CS1 were 38 percent ($p = 0.22$) and 16 percent ($p = 0.27$) higher than from CS2 (Table 3). For these events, runoff from CS2 was more than three times that from CS1. Interpretation of these values is not expected to be affected by the one day difference in herbicide application date between CS1 and CS2. If anything, it makes the CS2 loss a conservative estimate. In 1998, runoff from CS2 for the first three events was 102 percent

Table 5. Seasonal runoff, atrazine, and metolachlor losses measured from CS1, CS2, and CS5.

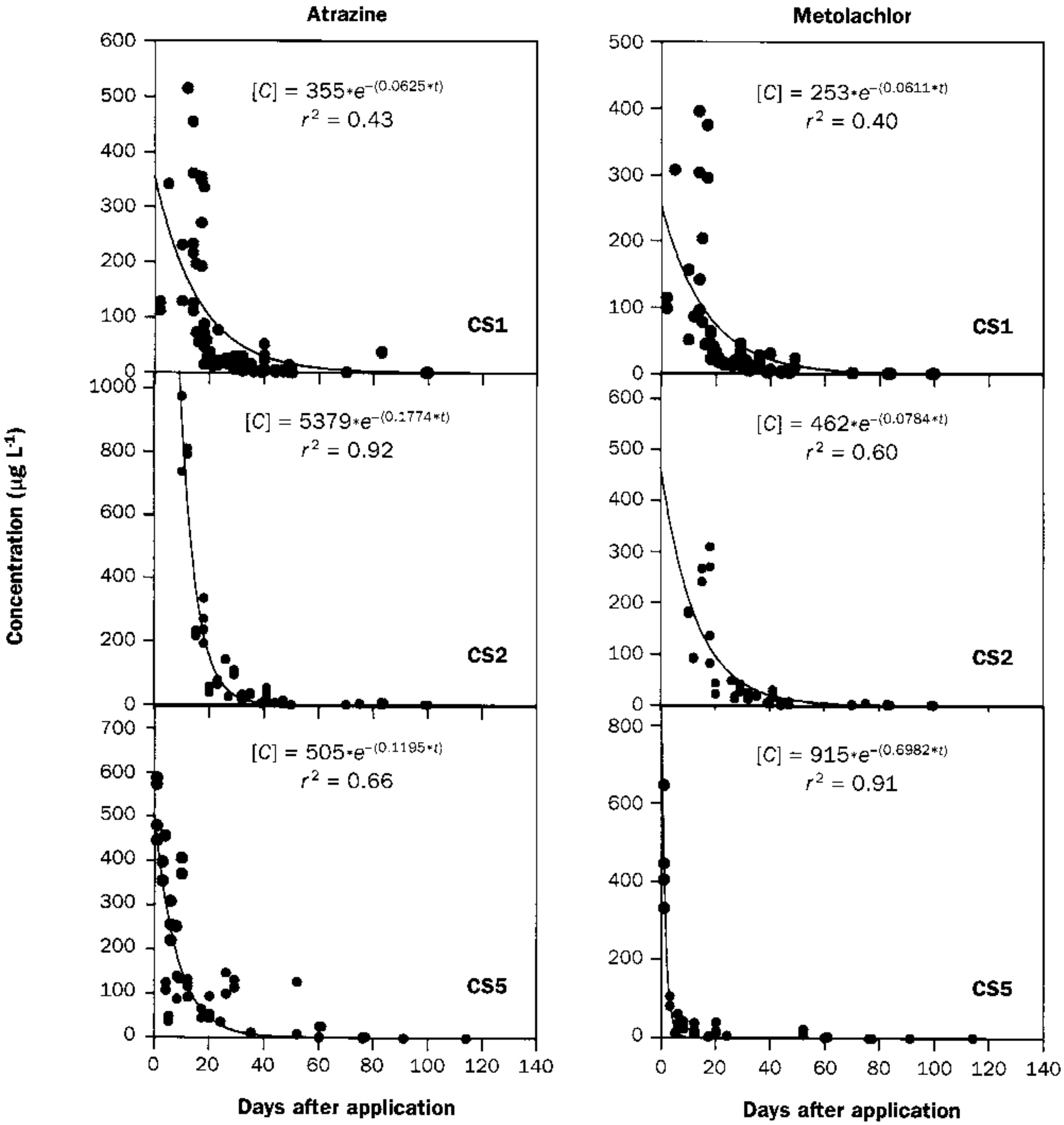
Year	Runoff, mm			Atrazine, g ha-1			Metolachlor, g ha-1		
	CS1	CS2	CS5	CS1	CS2	CS5	CS1	CS2	CS5
1997	11.8b*	43.9a	27.6b	24.4b	55.1b	85.3a	22.5b	61.9a	——
1998	49.6c	65.6b	87.5a	5.6b	42.6a	68.7a	5.9a	14.7a	——
1999	58.5a	57.6a	61.0a	13.1b	20.2b	29.5a	16.4a	12.5b	9.2b
2000	169.9a	164.5a	170.0a	33.8b	113.1a	93.0a	22.1a	29.6a	14.8a
2001	184.0	——	70.6	89.3	——	64.0	100.1	——	41.3
2002	8.7a	5.0b	4.2b	47.7a	43.6a	——	8.0a	4.8a	1.1a
Means†	59.7a	67.3a	70.8a	24.9b	55.0a	55.3a	15.0b	24.7a	8.4

† When an F-test Pr ≤ 0.10, LSD mean separation was performed (α = 0.10). Means within rows with different letters were significantly different.

. No data available for the parameter during the season.

† Mean values do not include data from 2001.

Figure 2
Atrazine and metolachlor concentrations in runoff as related to days after application.



(p = 0.20), 51 percent (p = 0.16), and 14 percent (p = 0.37) higher than from CS1. However, atrazine concentrations from CS2 were 323 percent (p = 0.20), 292 percent (p = 0.03), and 505 percent (p = 0.17) greater than from CS1 for these events. In 2000, runoff from both cropping systems was similar; however, atrazine concentrations from CS2 were higher than from CS1. For six of 10 events, the p-value was less than 0.10. For the others, the p value ranged from 0.11 to 0.77. In general, the study showed that herbicide concentration could be very high if a runoff event occurred soon after application for any cropping system. Once the temporal effect was accounted for, the study showed that herbicide incorporation reduced herbicide concentrations in surface runoff.

Event-based herbicide losses. For almost all the events, atrazine and metolachlor losses from CS2 were higher than CS1, but p-values for most of them were greater than 0.10 (Table 3). For some events, even though herbicide losses measured from CS2 were much

Table 6. Percent of atrazine and metolachlor applied transported in surface runoff.

Year	Atrazine, % applied			Metolachlor, % applied		
	CS1	CS2	CS5	CS1	CS2	CS5
1997	1.1	2.5	5.1	2.0	5.5	—*
1998	0.3	1.9	8.1	0.4	1.0	—
1999	0.6	1.0	1.0	1.2	0.9	0.8
2000	1.5	5.1	8.3	1.6	2.1	2.1
2001	4.0	—†	11.4	5.4	—	4.9
2002	2.1	2.0	0.0	0.4	0.3	0.1
Means	1.6	2.5	5.7	1.8	2.0	2.0

* Metolachlor was not applied to CS5 in 1997 and 1998.

† In 2001, atrazine and metolachlor concentrations were not measured from CS2 until 36 days after herbicide application.

higher than the losses from CS1, the p-values remained high. For instance, atrazine loss for the first event in 1998 from CS2 was more than 9 times higher than CS1, but the p-value was 0.27. Similarly, atrazine loss for the first event in 2000 from CS2 was four times higher than CS1, but the p-value was 0.28. These high values were caused by the limited replication (two replications) and high degree of variability associated with this experimental design. However, pooled over years (excluding 2001), average atrazine loss by event for CS2 was 9.6 g ha^{-1} (0.01 lb ac^{-1}) and approximately three times higher ($p = 0.03$) than for CS1. Average metolachlor loss by event for CS2 was 4.0 g ha^{-1} (0.003 lb ac^{-1}) and approximately two times higher ($p = 0.07$) than for CS1.

In 1997 and 1998, atrazine and metolachlor losses from CS2 were larger than those from CS1 because of larger runoff volumes from CS2. For the runoff measured in 1999 and 2000 from CS1 and CS2, the p values were greater than 0.10. However, atrazine losses from CS2 were much larger than CS1, particularly for the first few critical events. This indicates that under similar hydrologic condition, the greater herbicide loss to runoff from the no-till system was caused by lack of herbicide incorporation.

Seasonal herbicide losses. Herbicide losses from cropping systems where herbicides were surface applied and not incorporated (CS2 and CS5) were higher than those from a cropping system where herbicides were surface applied and incorporated (CS1) (Table 5). Averaged over the years, atrazine losses from CS2 and CS5 were 120 percent ($p = 0.08$) and 122 percent ($p = 0.06$), respectively, higher than those from CS1. Metolachlor loss to surface runoff from CS2 was 65 percent higher ($p = 0.01$) than that from CS1. Atrazine losses to surface runoff from CS1, CS2, and CS5 accounted for 1.6, 2.5, and 5.7 percent of the total applied to the soil (Table 6). Metolachlor losses from CS1, CS2, and CS5 accounted for 1.8, 2.0, and 2.0 percent of the total applied.

The effect of split herbicide application in a no-till system (CS2 and CS5) was also evaluated. In 1997, runoff from CS5 for the first two events, which occurred 10 days after the second application, was 30 percent lower than that from CS2. However, the atrazine loss from CS5 was 71.0 g ha^{-1} (0.063 lb ac^{-1}) compared to 8.0 g ha^{-1} (0.0071 lb ac^{-1}). Seasonal atrazine losses from CS5 and CS2 in 1997 were 85.5 and 55.1 g ha^{-1} (0.08 and 0.05 lb ac^{-1}), respectively, which accounted for 5.1 and 2.5 percent of atrazine applied in that year. In 1999, runoff from CS5 for the event that occurred 5 days after the second application was similar to that from CS2. However, atrazine loss from CS5 was 20.2 g ha^{-1} (0.018 lb ac^{-1}) compared to 12.0 g ha^{-1} (0.011 lb ac^{-1}) from CS2. Seasonal atrazine losses from CS5 and CS2 in 1999 were 29.5 and 20.2 g ha^{-1} (0.026 and 0.018 lb ac^{-1}) and accounted for 1.0 percent of that applied in both cropping systems, which indicates the larger loss could be explained by the higher application rate.

The effect of application rate on herbicide losses to runoff was also evaluated for the two no-till cropping systems, but different application rates in the presence of different timing limited the inferences that could be made. Atrazine applied to CS2 was 2.6 and 2.0 times that applied to CS5 in 1998 and 2000, respectively (Table 1). For these years, atrazine was applied to CS2 on the day of planting, whereas atrazine was applied to CS5 at 35 and 24 days after planting. In 1998, 8.1 percent of atrazine applied was transported in surface runoff from CS5 compared to 1.9 percent from CS2. Similarly, in 2000, 8.3 percent of atrazine applied was transported in surface runoff from CS5 compared to 5.1 percent from CS2. Even though atrazine applied to CS2 was 2.6 and 2.0 times that applied to CS5, the timing of the runoff events caused higher atrazine losses from CS5 compared to CS2, particularly in 1998. For instance, the first two runoff events in 1998 from CS2 occurred 18 and 23 days after application and approximately 20 mm (0.8 in) of total runoff was measured. For CS5, the first two events occurred four and nine days after application and approximately 48 mm (1.9 in) of total runoff was measured. For these events, total atrazine loss from CS5 was 74 percent higher than CS2. The study clearly showed that timing of runoff relative to application date was more critical in herbicide loss than application rate.

Overall, the study showed that incorporation, application rate, runoff volume, and timing of runoff event relative to herbicide application are important factors that affected the amount of herbicide transported to surface runoff. Further, for split applications, the interaction of these factors, particularly timing, make it difficult to predict the combined effect.

Modeling herbicide concentrations in runoff. The second objective of this work was to develop a quantitative relationship relating herbicide concentration to runoff volume, application rate, and days after application. Previous work has suggested that the factor of primary importance was time after application, as represented by Equation (3). The data obtained in this experiment were used to examine goodness of fit of that simple model.

Atrazine and metolachlor concentration data measured from the plots (not the mean values) were plotted against days after application and the simple exponential decay model (Equation 3) was fitted to these data (Figure 2). For CS1, the model did not fit well for either atrazine or metolachlor concentrations ($r^2 = 0.43$ for atrazine, $r^2 = 0.40$ for metolachlor). The model underestimated concentrations for the events with small runoff and very high atrazine or metolachlor concentrations. In 1997, two small runoff events (<3.5 mm) occurred 14 and 17 days after application and atrazine and metolachlor concentrations measured from CS1 were very high (Table 3). The low runoff volumes for these events might have contributed to the high concentration, which emphasizes the importance of including a runoff parameter to the simple model. The model also underestimated atrazine concentration in CS1 for an event that occurred 12 days after application in 2002 where measured runoff and atrazine concentrations were 8.9 mm and 514 μg L^{-1}, respectively, compared to the estimated atrazine concentration of 168 μg L^{-1}. The correlation of the model for atrazine and metolachlor from CS1 greatly improved when these outliers were excluded ($r^2 = 0.65$ for atrazine and $r^2 = 0.60$ for metolachlor). The correlation of the model was good for atrazine concentration from CS2 ($r^2 = 0.94$) and metolachlor concentration from CS5 ($r^2 = 0.94$); however, the intercept values (C_o) were very high (4717 μg L^{-1} for CS2 atrazine, and 915 μg L^{-1} for CS5 metolachlor) indicating strong sensitivity to a few high-concentration events that occurred soon after application. Because the model (Equation 3) is only a factor of time elapsed after application, its use could be limited, particularly in a situation when there is a variation in runoff volume and application rates.

For the generalized equation (Equation 4), the non-linear procedure of SAS (Proc NLIN) was run to estimate the coefficients *a* and *k* for both atrazine and metolachlor in each cropping system. In this analysis, runoff and concentrations data measured from the individual plots (not the mean values reported in Tables 3 and 4) were used. Data measured for the events that occurred after the second herbicide application day for CS5 were not used in this analysis. The model performed quite well in determining the coefficients for both CS1 and CS2. However, Proc NLIN would not converge to a good relationship between measured and calculated concentrations for CS5. The model was not able to correctly estimate when there were multiple events in one day, especially when the runoff from the second event was much lower than the first event. For the events that occurred on the same day, herbicide concentration from the first event was expected to be much higher than those from the following events. Several studies reported that herbicide concentration in runoff was highest in those samples taken soon after runoff initiated and decreased rapidly (Hall et al., 1983; Pantone et al., 1992). Because the model includes a runoff parameter, for events that occur on the same day, concentration from a small runoff event will be much higher than that from a large runoff event, particularly if the event occurs within a few weeks after application. To avoid this problem (particularly for CS5), Proc NLIN was run again for the runoff events > 2mm. For CS5, this greatly improved the performance of the model. The coefficients generated by this procedure are given in the equations below. For CS1, the following equations were developed:

$$[Atr] = 0.0232 \times \left(\frac{R}{Q}\right) \times e^{-(0.1087 \times t)} \qquad (7)$$

$$r^2 = 0.68$$

$$[Metol] = 0.0203 \times \left(\frac{R}{Q}\right) \times e^{-(0.0862 \times t)} \qquad (8)$$

$$r^2 = 0.71$$

For CS2, the equations were:

$$[Atr] = 0.0959 \times \left(\frac{R}{Q}\right) \times e^{-(0.1412 \times t)} \qquad (9)$$

$$r^2 = 0.80$$

$$[Metol] = 0.011a \times \left(\frac{R}{Q}\right) \times e^{-(0.0678 \times t)} \qquad (10)$$

$$r^2 = 0.23$$

For CS5, the equations were:

$$[Atr] = 0.0383 \times \left(\frac{R}{Q}\right) \times e^{-(0.1505 \times t)} \qquad (11)$$

$$r^2 = 0.70$$

$$[Metol] = 0.0239 \times \left(\frac{R}{Q}\right) \times e^{-(0.2838 \times t)} \qquad (12)$$

$$r^2 = 0.76$$

where,

[Atr] = are calculated atrazine concentrations in μg L^{-1}.

[metol = are calculated metolachlor concentrations in μg L^{-1}.

Accounting for the additional factors of runoff volume and application rate complicates the presentation of the data. There is no simple presentation of a three-parameter model such as Equation (4). However, if Equation (4) is rearranged as in Equation (6) to obtain herbicide loss relative to application rate, it can be visualized as a simple function of time. Thus, for each cropping system, the performance of the model was illustrated by plotting percent of atrazine and metolachlor applied lost to surface runoff against days after application (Figure 3). Equation (6) has greatly improved performance for CS1 compared to the simple exponential decay model (Equation 3). The model performed quite well in estimating relative atrazine losses from CS1 ($r^2 = 0.68$), CS2 ($r^2 = 0.80$), and CS5 ($r^2 = 0.70$). The model also performed well in describing relative metolachlor losses from CS1 ($r^2 = 0.71$) and CS5 ($r^2 = 0.76$); however, model performance in describing metolachlor from CS2 was poor ($r^2 = 0.24$).

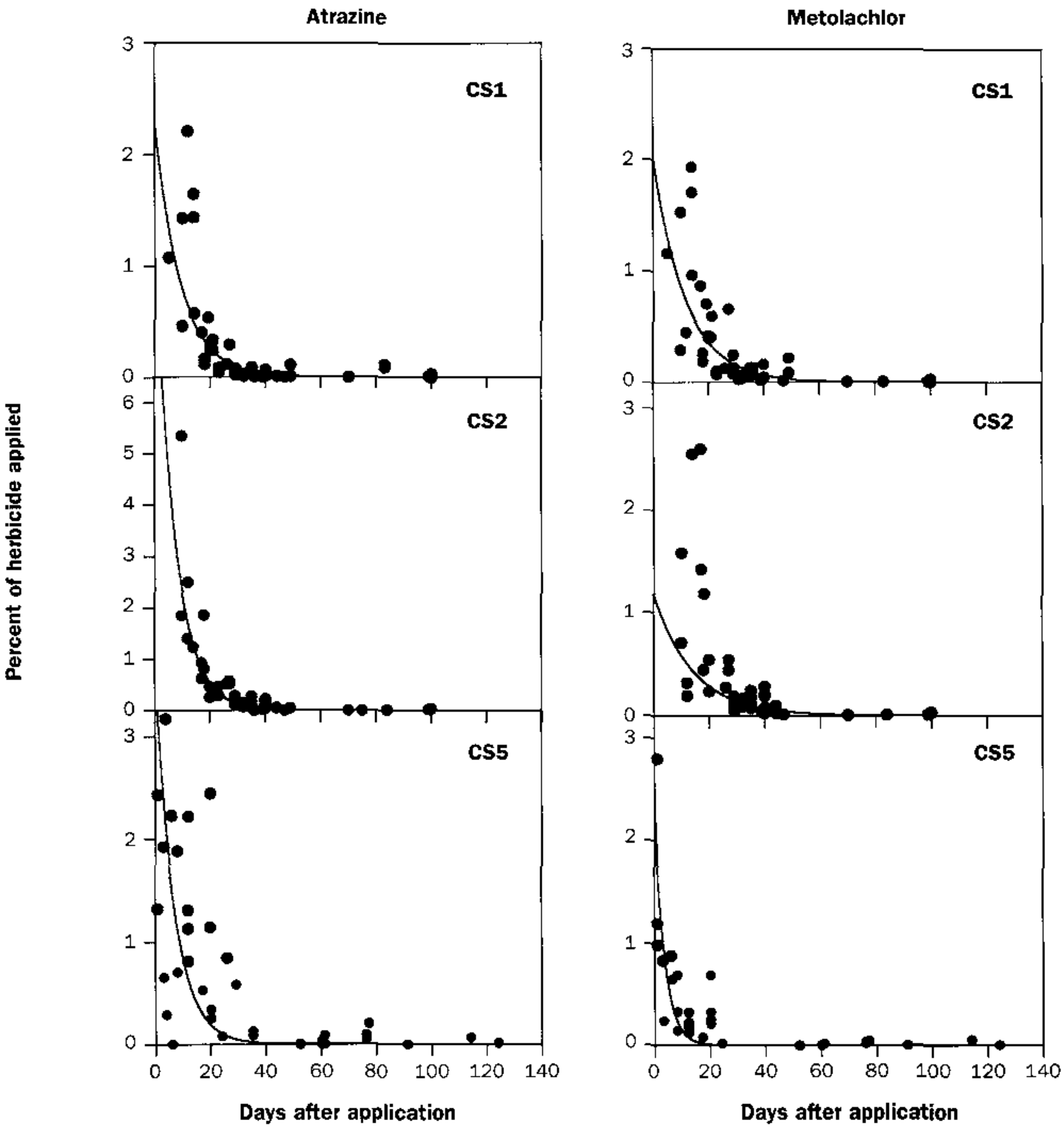
While the presentation of relative herbicide loss as a function of time can be easily visualized, it doesn't address the goodness of fit in the familiar terms of concentration. The way we chose to represent this is to plot residual errors of the model against measured concentrations. A residual error is defined as the difference between estimated and measured concentration values. This is not a test of the model; it is solely a representation of the goodness of fit to the concentration data that was used to develop the coefficients. A rigorous test of this model using independent data sets will be the subject of later research. Plots of residual errors against measured atrazine and metolachlor concentrations from CS1, CS2, and CS5 are shown in Figure 4. Although the performance of the model in estimating atrazine and metolachlor concentrations was good (except for metolachlor from CS2), there were a few events with high measured concentrations where the model, in most cases, underestimated the concentrations which resulted in large magnitude, but negative, residual error values. For instance, for an event that occurred 12 days after application in 2002 from CS1, measured and calculated atrazine concentrations were 514 and 126 μg L^{-1} with a residual of -388 μg L^{-1}. By considering flow and herbicide application rate, this model represents a more generalized model for estimating herbicide concentration that should be applicable over a wide range of scales.

Summary and Conclusion

Herbicide transport in surface runoff was measured from three cropping systems located in the claypan soil region of north-central Missouri from 1997 to 2002. Herbicide losses

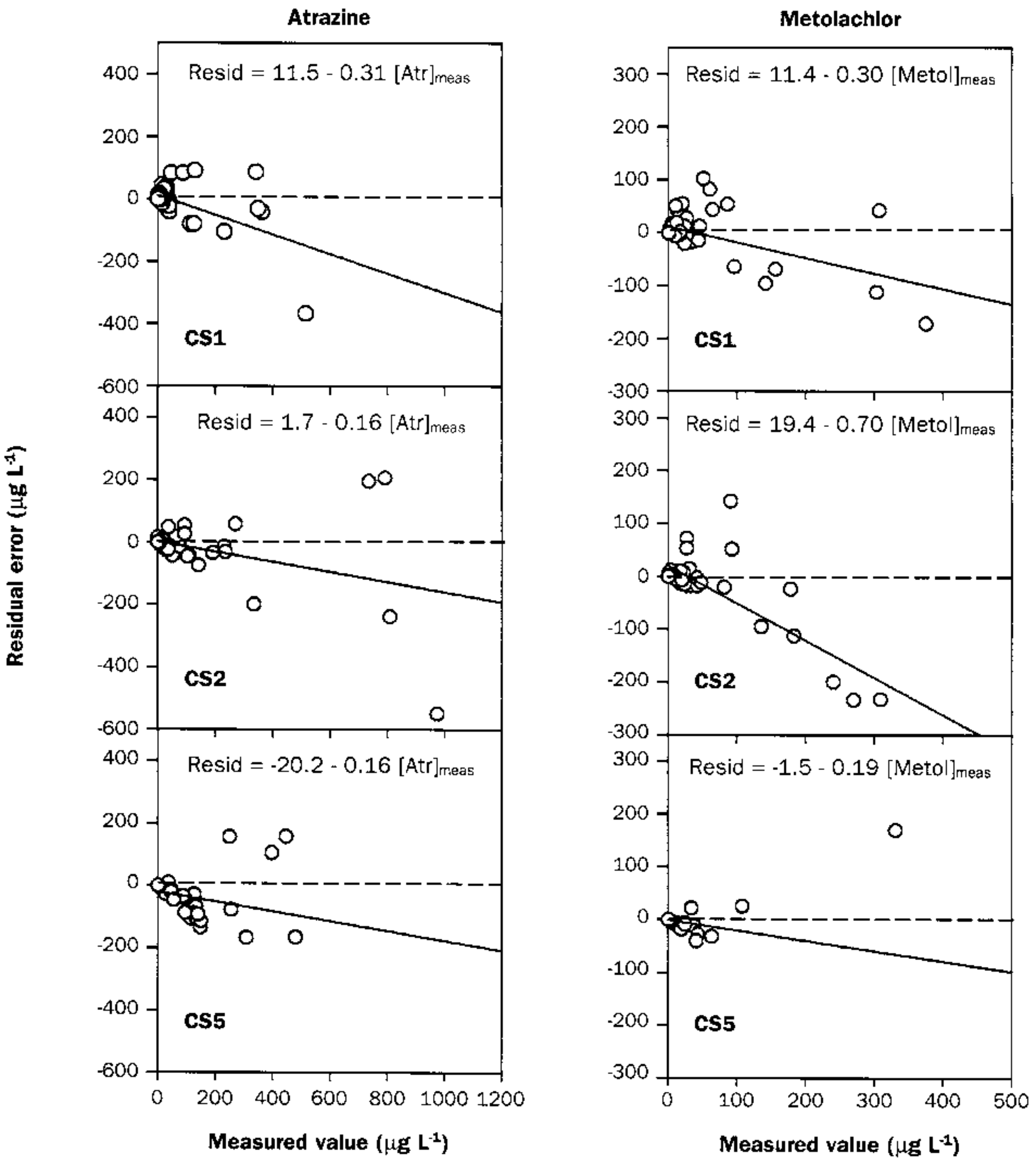
Figure 3

Percent of atrazine and metolachlor applied transported in runoff as a function of days after application. Note that the scale for atrazine in CS2 is twice that of others.



measured from CS2 and CS5 (no-till systems) were 120 percent ($p = 0.08$) and 122 percent ($p = 0.06$), respectively, higher than those measured from CS1 (mulch tillage). Under similar herbicide application and hydrologic conditions, atrazine and metolachlor losses from no-till were two times higher than from mulch tillage. Split atrazine application in no-till further increased atrazine loss in surface runoff by creating two vulnerable periods for surface transport during the critical loss period. Throughout the study period, 1.6, 2.5, and 5.7 percent of the total atrazine applied to CS1, CS2, and CS5, respectively, was lost to surface runoff. Also, 1.8, 2.0, and 2.0 percent of the total metolachlor applied to CS1, CS2, and CS5, respectively, was lost to surface runoff. Herbicide concentrations in surface runoff were extremely high for the runoff events that occurred within a few days of application. A generalized model for estimating herbicide concentration was developed based on the exponential decay in observed concentration combined with flow

Figure 4
Residual errors of the model plotted against measured atrazine and metolachlor concentrations, for the calibration data set.



and application rate. The utility of this model will be tested at larger scales from field case studies in the near future.

This study showed that herbicide losses to surface runoff mainly occurred within a 60-day period after application and were much higher when herbicides were not incorporated. Thus, for runoff-prone soils, such as the Central Claypan Area, no-till systems create a particularly vulnerable setting for surface transport of soil-applied herbicides because of lack of herbicide incorporation. Tillage systems, such as no-till, that leave residue on the soil surface are quite effective management systems in reducing soil loss, which is the primary reason for no-till adoption on these soils. However, a key management challenge is finding a management practice that both minimizes soil erosion and reduces herbicide loss to surface runoff.

Footnote

[1]Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

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